Understanding the Structural and Chemical Basis of Chalcopyrite Solar Cell Operation

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Previously, we have reported on the micro-structure and micro-chemistry of *industrial* samples provided by Global Solar Energy (GSE) and Shell Solar Industries. Differences between the two materials were found, and the initial results were summarized in a paper published in the proceedings of the MRS 2003 spring meeting in the session on Compound Semiconductor Photovoltaics (copy attached).

Recently, we received and have begun to study three kinds of samples from IEC, University of Delaware. The growth procedure and resulting efficiencies of devices produced from each sample are different, and are different from the *industrial* films. All samples except the Shell Solar sample were received as completed devices with CdS junctions patterned, and transparent oxide coatings. The work of this quarter concentrated on IEC sample 1 (No. 33505) and the second GSE sample (Sample No. 809SA). Because of weak adhesion between the film and Mo-buffer layer sputtered on glass, a careful sample preparation process involving the use of a low-speed wire saw was developed to allow preparation of cross-sectional and plan-view samples.

1. Microstructure & microchemistry of IEC sample 1 (No: 33505)

Figure 1a is a typical TEM bright-field image. It gives an overview of the IEC film morphology. The film is not fully dense and shows voids of different sizes. The typical grain-size varies from 0.1μm to 0.8μm, with most being around 0.4μm, proving once again that large grain sizes are not necessary to obtain good device performance (near 14% in this case). Both the number and volume of voids in IEC sample 1 are higher than those of GSE sample 1, which was studied previously and the results presented in a previous report. Inside the grains some parallel fringes were observed due to twins or stacking faults. These planar defects are frequently observed in CIGS samples. Dislocations are occasionally found in a few grains. The number of dislocations varies from several to many within these grains. Figures 1b and 1c show two grains with different dislocation densities. No direct correlation between grain size and dislocation density was discerned. Ongoing studies will examine any compositional difference between the grains with high and low dislocation densities.

The chemical measurements from more than 120 positions (with the typical beam-diameter of about 5nm) are summarized in figure 2a. No significant impurities such as O or Na were found inside the grains. The average composition (atomic percentage) is 24.5%Cu, 7.3%Ga, 52.1%Se, 16.2%In, which is quite close to the composition provided by IEC, 23.5%Cu, 9.3%Ga, 49.2%Se, 18.0%In. Figure 2b is an enlargement of the data plotted in figure 2a, and shows the composition of this CIGS film is slightly off-stoichiometry. Fitting of the results shows that the data points lie along a line connecting stoichiometric $Cu(InGa)Se_2$ and $CuSe_2$. This is not a normal tie line of the ternary phase diagram and indicates a loss of In without a change in the Cu/Se ratio. This off-stoichiometry may be attributed to an inhomogeneous microstructure caused by an inefficient annealing treatment, or to the loss of In during sample preparation (In is easily removed during ion milling). Further microchemical analysis on cross-sectional samples will be performed in the next funding period to determine if this is a real effect.

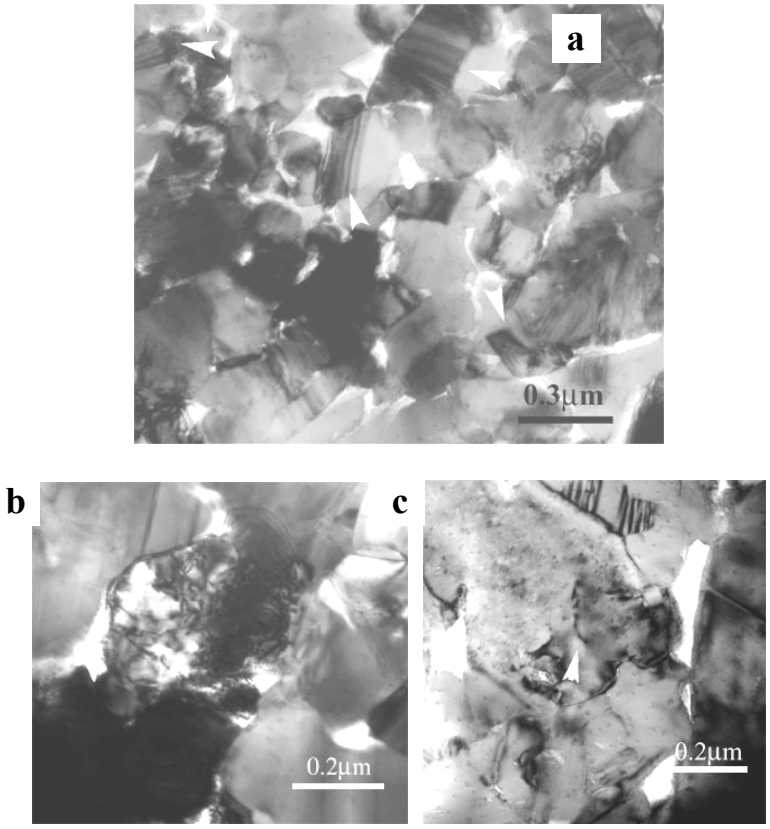

Figure 1. The microstructure of IEC sample 1 (33505). (a) An overview image showing the high density of voids, at grain boundaries. White arrows mark the possible twins and stacking faults. Two enlarged images showing the grains containing of (b) many of and (c) several dislocations.

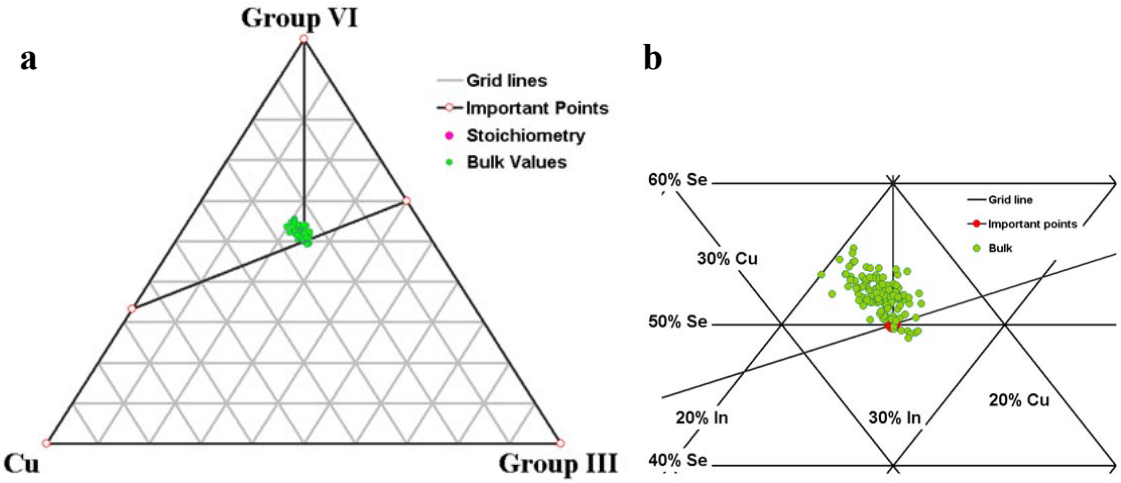

Figure 2 The bulk composition of CIGS film. (a) 120 points probed inside of the grains are plotted in a ternary phase diagram. (b) is the enlargement of the data shown in (a), revealing that the film composition is slightly In deficient.

EDS line scans were performed to study the local composition variation at the grain boundaries. Figures 3a and 3b present two typical images in which the microchemistry crossing grain boundaries was probed. Figures 3c and 3d show the elemental variation along the probe line. CdS was obviously found at the grain boundary of figure 3c, but not in figure 3d. No significant CdS was found inside the grains in both figures 3a and 3b, indicating that

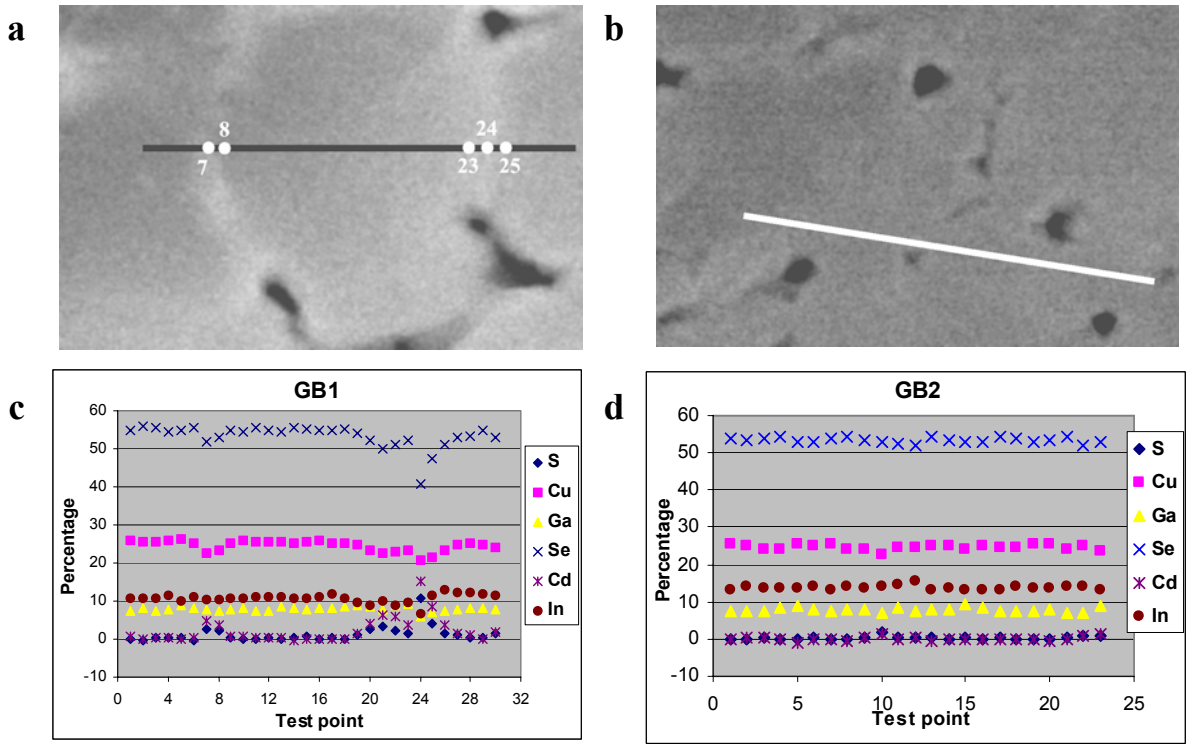

Figure 3 Line scan cross the grains and grain boundaries. (a) and (b) are two typical images. (c) and (d) are corresponding composition. CdS was found in the GBs of (a) and (c) whereas not in (b) and (d). The probe locations are along the line, but could not be identified individually because of their number.

these elements do not diffuse into the grains significantly even when a thin CdS volume is present in grain boundaries.

Figure 4 presents the charts revealing correlations between Cd and S, and other elements (Ga, In, Se, Cu). No strong correlations between Cd and elements Ga, In, Se, or Cu were revealed. In addition, no correlations between S and other elements were revealed. However, it was found that there is a significant correlation between S and Cd: the Cd L percentage increases with the S K percentage almost linearly but with a ratio of 2 Cd atoms per S atom. There is no significant correlation of Cd with Se, indicating that Se is not compensating for the loss of S. A further study of the microchemistry on the cross-sectional samples, in particular at the areas close to the CdS/CIGS interface is required to understand the CdS at grain boundaries.

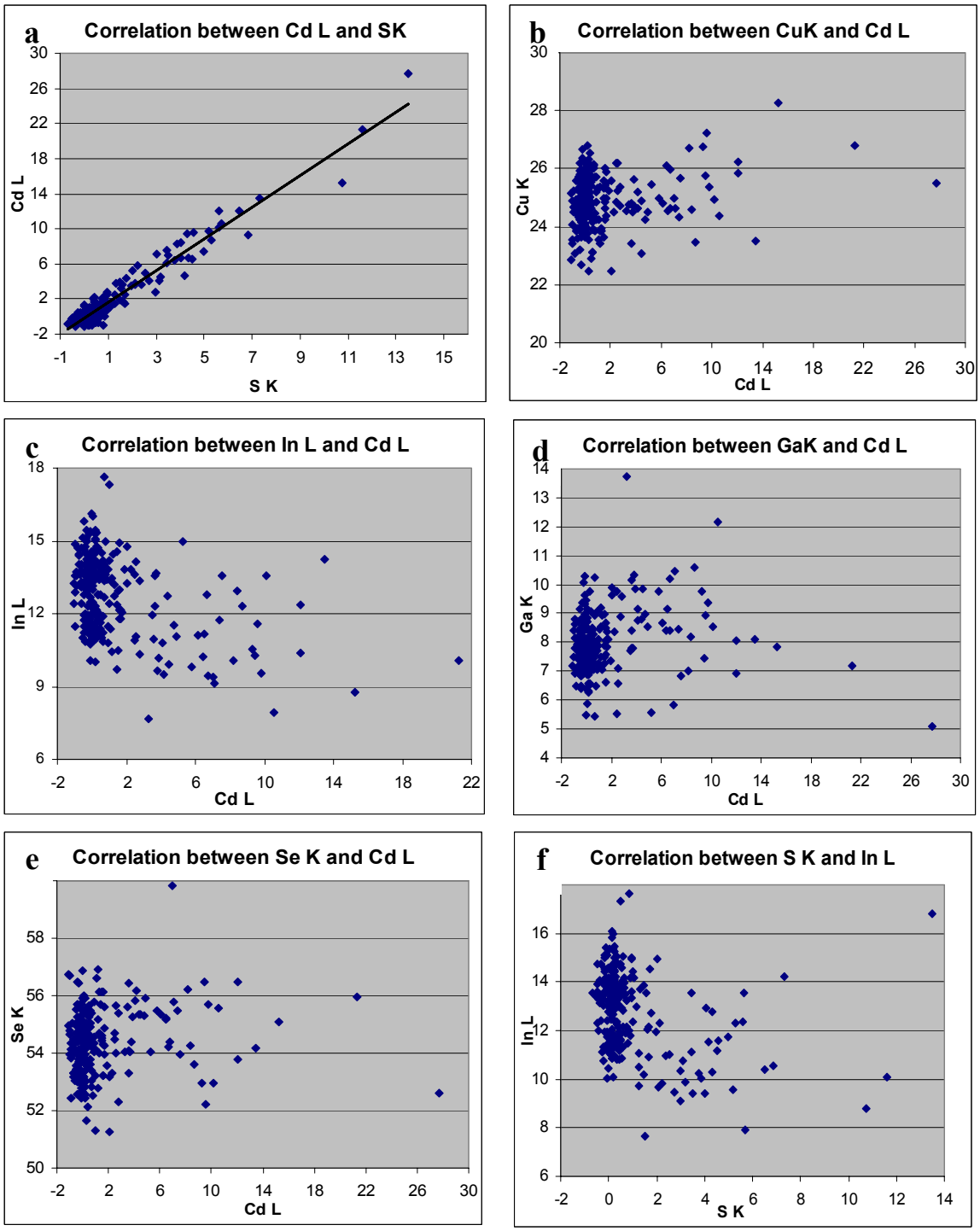

Figure 4. The correlation of (a) Cd L and SK, (b) Cd L and Cu K, (c) Cd L and In L, (d) Cd L and Ga K, (e) Cd L and Se K, and (f) S K and In L.

2. Microstructure of GSE sample 2 (sample number 809SA)

Figure 5a presents a plan-view image of sample 809SA. This microstructure is similar to the GSE sample 1 that was reported previously. The film is much denser than that of the IEC sample 1. Moreover, the typical grain-size varies from 0.5μm to 1.2μm, most being close to the 1μm level. Hence, the grains in the GSE sample are bigger than those of IEC sample 1. Inside the grains twins and stacking faults are found, as indicated by the white arrows. These observations are consistent with those reported previously for sample 1. Electron diffraction reveals that the film is well ordered. The evidence is shown in figure 5b, which is the [112] pattern (the index is based on diamond structure) of CIGS. The superlattice spots in figure 5b are strong and sharp, revealing good ordering of CIGS grains.

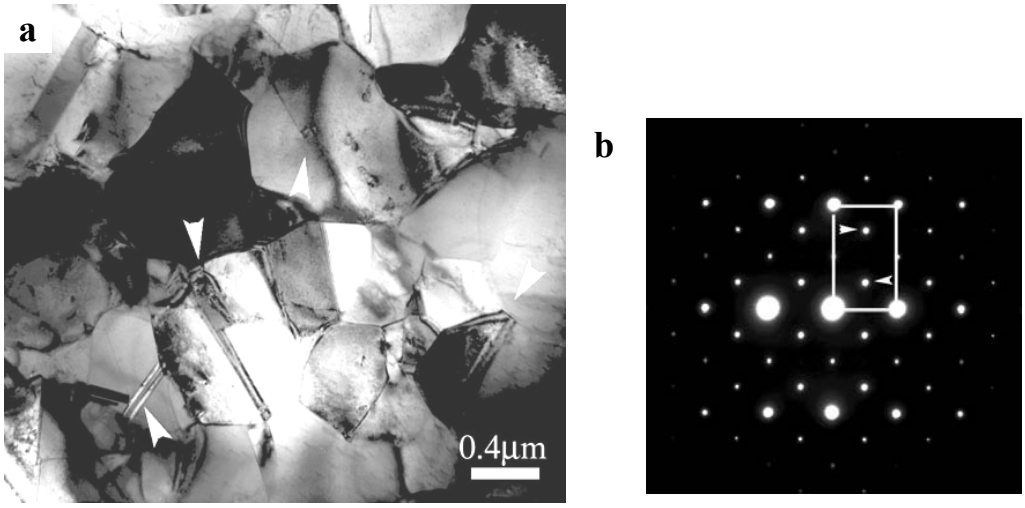

Figure 5. (a) A TEM bright field image showing the microstructure of CIGS films. (b) is an electron diffraction pattern recorded from one grain. The white frame marks the unit cell of diamond structure while arrows mark the superlattice spots resulting from the order of CIGS. The strong and sharp superlattice diffraction spots reveal the good degree of ordering.

3. Summary and future work

It is important to compare the different samples and identify any microstructural and microchemical variations that could explain the variation in performance. Table 1 summarizes the information of three kinds of films we are investigating.

Table1: Comparison of three kinds of samples investigated in this work

	Shell Sample	GSE sample1 (823SB)	IEC sample1 (33505)
Structure	CIS/Mo/Glass	Oxide/CdS/CIGS/Mo/SS	ITO/CdS/CIGS/Mo/Glass
Efficiency	14%	11%	13.7%
Annealing T	550ºC	550ºC	400ºC
Preparation	Single stage	Two stages	Two stages
Microstructure	1:Grain size near 1 um 2:Dense film free of voids	1:Grain size: near 1um 2: Occasional voids in both grains and at grain boundaries	1:Grain size 0.5um 2:High density of voids, in particular at GB areas
Composition	1:$CuInSe_2$ 2: Impurities: O	1:$Cu_{19.7}(InGa)_{28.2}Se_{52.1}$ 2:Impurities: Na,O	1: $Cu_{24.5}(Ga_{7.3}In_{16.2})\ Se_{52}$ 2: CdS at GBs

Based on the results we have obtained and questions encountered, our plans in the next funding period are as follows.

(1) To repeat to compositional analysis of plan-view and cross-sectional samples of the Shell Solar Industries material in order to verify the different behavior of oxygen, sodium and selenium between grain interiors and grain boundaries. Microchemical analysis of additional grain boundaries in both plan and cross-sectional view samples of the Global Solar Energy will be performed to confirm the initial observations.
(2) To prepare the plan-view and cross-sectional samples of the other two IEC samples, and determine the microstructure and microchemistry.
(3) To compare the composition gradients of IEC samples and GSE samples in order to understand how the growth temperature and preparation methods can affect the equilibrium of film microstructure.
(4) To study the interfacial microchemistry between CdS and CIGS.